DESIGN, SYNTHESIS AND CONTROLLING THE ANION SELECTIVITY OF SYNTHETIC RECEPTORS

A SYNOPSIS

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1. INTRODUCTION

Anions, such as F^-, CH_3COO^-, and $H_2PO_4^-$ play an important role in many biological processes and are involved in agricultural fertilizers and food additives. Anions have lethal effects on the environment [1]. Anions are crucial to biology and medicinal research, yet they are also destructive to the environment and a major source of environmental pollution. Eutrophication is treated as one type of environmental pollution [2]. Fluoride ion is one of the anions that are of great importance due to its involvement in preventing dental cavities and treating osteoporosis [3]. An elevated amount of fluoride in drinking water causes dental and skeletal fluorosis [4]. Chloride has a major physiological significance, which includes regulation of osmotic pressure, electrolyte balance, and acid-base homeostasis. Chloride is present in all body fluids. In a similar way, iodide is crucial for proper thyroid function. For nutritional, metabolic, and epidemiological research of thyroid dysfunction, the iodide level of urine and milk is frequently necessary [5].

The construction of anion receptors is an extremely demanding area of sensory research [6–20]. In particular, designing the selective colorimetric sensor toward a specific anion is always challenging for researchers. The anion receptor requires a combination of hydrogen bond donor groups and the anion receptors contain a suitable framework on which various structural elements can be put together. At this juncture, we have designed and synthesized electron-deficient bipodal, tripodal and bicyclic receptors. Many reports have shown the possibility of complexation between the pi cloud of pentafluoro substituted aromatic system and electron-rich molecules such as anions [21-22]. Bryantsev and Hay *et al.* observed that, the electron-withdrawing substituent on the aromatic systems appreciably increases the stability of anion-ligand complexes [23]. In this research scenario, we have designed the receptors for the selective recognition of biologically and environmentally significant anions, including cyanide, azide, acetate, fluoride, dihydrogen phosphate, and bifluoride anions.

2. REVIEW OF LITERATURE

Supramolecular chemists were designing various types of receptors to achieve selective recognition of anions. Park and Simmons *et al.* reports first macrocyclic anon receptors based on electrostatic interactions [24]. After nine years, Franz and Schmidtchen

et.al. reported another report which was macrocyclic cage based on electrostatic interaction [25]. Reinhoudt *et al*. designed first neutral tripodal receptors with hydrogen donors and received successful interaction with anions [26]. Bryans and Hay *et al.* report reveals electron withdrawing substitution on the receptor structure can enhance the acidic nature of the hydrogen donors [23]. Ghosh *et al.* report revealed the influence of nitro substitution on orientation of the receptor by self-assembly with anions [27]. Shao *et al.* approached anions with nitrated phenylhydrazine based receptors [28]. Electron withdrawing groups substituted aryl rings brings electron deficient positive charge zone to anions which can be called as π-hole electrostatic interaction. Schneider *et al.* published first report regarding anion - π interaction at 1993 [29]. Lakshminarayanan *et al.* designed tripodal frame to better encapsulation via π-hole-anion-π-hole interactions. Tris(2-aminoethyl) amine used to construct tripodal frame with fluorinated and non-fluorinated phenyl rings [22].

3. OBJECTIVES

1. Design and syntheses of simple, effective, colorimetric, and fluorescent anion-selective receptors for environmental and biologically relevant anions.
2. Anion binding studies of anion-selective receptors:
   (a) Naked-eye colorimetric sensing studies
   (b) UV-Vis and Fluoro spectrometric studies
   (c) ^{1}H-NMR, FT-IR, and Molecular electrostatic surface analysis (MEP) of above-synthesized receptors and those anionic complexes.
3. Fabrication of receptors towards practical applications.

4. RESEARCH PROBLEM

Design and synthesis of Colorimetric and fluorescent receptors for Selective recognition of biologically and environmentally important anions. To achieve these objectives of the thesis, all possible experimental and spectroscopic studies are done and discussed in detail.

5. ORGANIZATION OF THESIS

The thesis entitled “DESIGN, SYNTHESIS AND CONTROLLING THE ANION SELECTIVITY OF SYNTHETIC RECEPTORS”. The thesis is composed of eleven chapters.

The research presented in this thesis show hydrazine-based imine, urea, thiourea, amide, and sulfonamide functionalized receptors having electron-withdrawing natured substituents at phenyl moiety show binding towards cyanide, fluoride, acetate, azide, dihydrogen phosphate and bifluoride anions.

Chapter I contains a general introduction of the thesis and a literature survey of previous studies of the anion receptors has been reported and the objectives of the current work are discussed. Chapter II deals with the experimental methods and procedures discussed in detail. Chapter III to X describes the results and discussion about the as-prepared receptors. Chapter XI discusses the summary of the work done in this thesis.

Chapter I: Introduction

Designing of selective colorimetric and fluorescent sensor towards a specific anion (which is environmentally and biologically relevant) is always challenging for researchers. The selectivity of a receptor with anion might be affected by in the presence of other traces. In host-guest chemistry concept, the receptor molecules must possess the recognition site that is particularly composed of hydrogen-bonding groups. Geometrical structure of the receptor is a crucial consideration when designing a receptor in order to obtain selectivity. Increasing the sensitivity increases the likelihood of anion attraction, which lowers the receptor's selectivity, which is another significant problem with creating selective and sensitive receptors. Geometrical structure and directional property of the H donor receptor component in the sensor molecule were given significant thought during our design and synthesis in order to resolve these sensitivity and selectivity relationships. Benjamin P Hay *et. al* has theoretically proved that the substitution of electron-withdrawing moiety on the aromatic ring of a chemosensor will improve the selectivity and sensitivity. From this concept, we have designed and synthesized different substitutions of electron-withdrawing groups to study their substituent effect on the anion sensing process, including color changes, and the selectivity and sensitivity of the anions. Interestingly, among all the synthesized receptors from L to L^{13}, the receptors are highly capable of detecting F^-, CN^-, FHF^-, N_3^-, AcO^-, and $H_2PO_4^-$ ions present in the form of TBA salts in the acetonitrile and DMSO over other anions due to their strong basicity and presence of strong electron-withdrawing nitro and fluoro substitutions in the framework of the receptors, which

increases the acidity of the binding site.

Chapter II: Review of Literature

Chapter 2 discussed the literature survey about the design and development of colorimetric anion sensing is even more significant and these reports helped to develop designing the anion receptors, but a perfect sensor should fulfill the selectivity, sensitivity, colorimetric and fluorescent signal.

Chapter III: A molecular phototropic system for cyanide: Detection and sunlight driven harvesting of cyanide with molecular sunflower

The directional motions of a plant in response to sunlight are called phototropism. It is named "phototropism" because it is a response to light rather than the sun. Herein we proposed a phenomenon called "molecular phototropism" in which the organic molecules undergo structural or confirmation change in response to (sun)light. Here we designed and synthesized a simple, easy to prepare, and conformation switchable first molecular phototropic system L^1, for cyanide harvesting. A reference compound L was also prepared without nitro substitution on the phenyl ring, which is very much intact with any anions as well as does not show such characteristics of L^1.

The sensing ability of L^1 is examined by the addition of Tetra butyl ammonium salts of various anions into the acetonitrile solution of L^1, individually. The color of the receptor L^1 was turned into dark pink color and faint brown in colors upon addition of cyanide/fluoride/acetate and bifluoride respectively. The formed cyanide complex is denoted as complex 1. Further, upon exposure of this transition state cyanide complex 1, under sunlight, this system is capable to release the bound cyanide via –C=N- free rotation to reach its lower energy stable conformation as shown in Figure 1. Similar behaviors were observed for acetate and fluoride with L^1. The strength of the phototropic system L^1 towards cyanide, acetate, and fluoride is found to be 4.5×10^5, $1.53 \times 10^{2,}$ and $6.09 \times 10^2 M^{-1}$. The cyanide complex of Schiff-base, L^1 is going back to the original conformation of L^1 from the conformation of cyanide complex 1 upon addition a water drop since water is able to break the -NH···CN hydrogen bonds between the L^1 and cyanide with our disturbing its conformation. The molecular sunflower can bind and sense the cyanide anion colorimetrically through its transition state, further upon exposure of this transition state

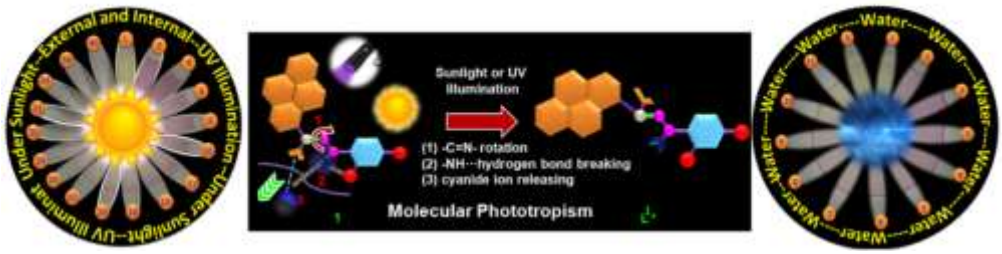

Figure 1: Graphical abstract of Molecular Sunflower

cyanide complex under sunlight, this system is capable to release the bound cyanide via –C=N- free rotation to reach its lower energy stable conformation state.

Chapter IV: Pyrene-Hydrazone-π···Hole Coupled Turn-on Fluorescent and Naked-Eye Colorimetric Sensor for Cyanide: Role of Homogeneous π-Hole Dispersion in Anion Selectivity

Constructing a synthetic chemo sensor is demanding area of sensory research. It is very clear from this and earlier results that fluorinated benzene plays a vital role in the selectivity of anion receptors. With this background, we have designed a pyrene-hydrazone-based receptor L^2, 2,3,4,5,6 pentafluoro substituted electron deficient benzene ring turn out to be a completely active receptor site by its π-holed character. Hence, the pyrene becomes only active signaling unit causes the photo-induced electron transport. In this report, the receptor L^2 sense exclusively cyanide anion via Photo Electron Transfer (PET) mechanism. The receptor L^2 shows a weak fluorescence emission spectrum which is mainly attributed due to the transfer of electron pair from the hydrazone nitrogen (-NH) into highly conjugated pyrene fluorophoric unit.

The cyanide selectivity with chemosensor L^2 is achieved by attaching 2,3,4,5,6 pentafuoro phenyl moiety into a pyrene-hydrazone compartment. The homogeneous dispersion of positive π···hole created by the pentafuoro moiety plays a vital role in the exclusive cyanide selectivity by L^2 which is depicted in Figure 2. Such a positive π···hole homogeneous dispersion is missing in the case of sensor L^2, instead, we have polarized π···hole dispersion towards 2^{nd} and 4^{th} position of the di-nitrophenyl chromophoric unit in L^1.

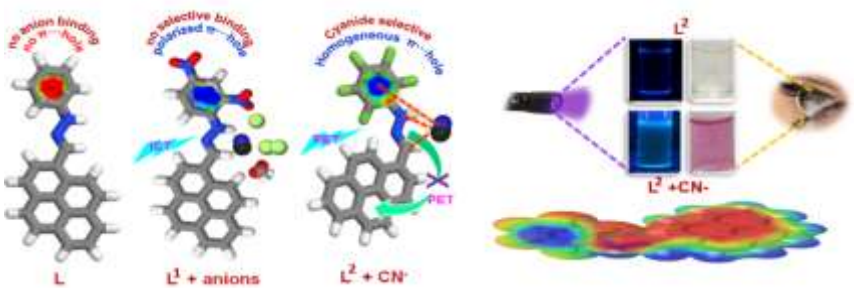

Figure 2: Graphical abstract of selectivity of cyanide with PET

Chapter V: Electron deficient imine-based receptor for selective colorimetric recognition of cyanide ion through aromatic CH•••anion interactions

Recently we reported a synthetic receptor in which the selectivity of the receptor towards cyanide is achieved by functionalizing the aromatic moiety with electron withdrawing natured nitro groups. Here in, we are reporting a simple, electron deficient, cost effective and easy to prepare imine-based selective colorimetric receptor for cyanide ion which is one of the hazardous anion in any forms.

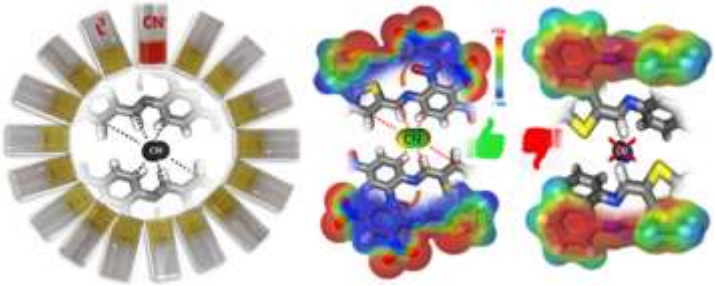

Figure 3: Graphical abstract of cyanide recognition via non-traditional interaction.

Naked-eye colorimetric experiment and UV–vis spectrometric studies reveal that the receptor L^3 selectively binds the cyanide anion through C–H•••cyanide interaction. The binding stoichiometry of the cyanide complex of L^3 is found to be 2:1 (L^3: CN^-) and the association constant and detection limit of complex 1 with cyanide is found to be 0.058×10^2 M and 4.12×10^{-6} M^{-1} respectively. The calculated association constant is relatively low this might be due to the participation of non-traditional aryl C–H•••cyanide interactions instead of than traditional hydrogen bond donors such as amide, amine, urea,

etc. Selectivity is the main factor that will highlight any chemosensor.

The electron-withdrawing natured functionalization on the aromatic moiety of L^3 is significantly enhanced the strength and selectivity of anion sensor L^3. Particularly, upon nitro substitution at 2nd and 4th phenyl ring of L^3, the unsubstituted aromatic –C–H groups are rehabilitated into relatively more acidic i.e. The aryl group having nitro functionalities that contribute to selective anion binding in cyanide complex of L^3 through CH•••cyanide ion interaction and here were no traditional hydrogen bondings donors are associated with receptor L^3, the preferential cyanide binding by receptor L^3 predominantly attributed due to enriched aromatic C–H•••anion and imine-CH•••anion interactions are shown in Figure 3. To the best of our knowledge, this is the first report of colorimetric sensing of cyanide majorly inclined by non-traditional Aromatic-C–H•••cyanide interaction.

Chapter VI: A Molecular Swan: Naphthalene-hydrazone based $\pi\cdots$hole coupled electron-deficient naked-eye selective colorimetric cyanide sensor

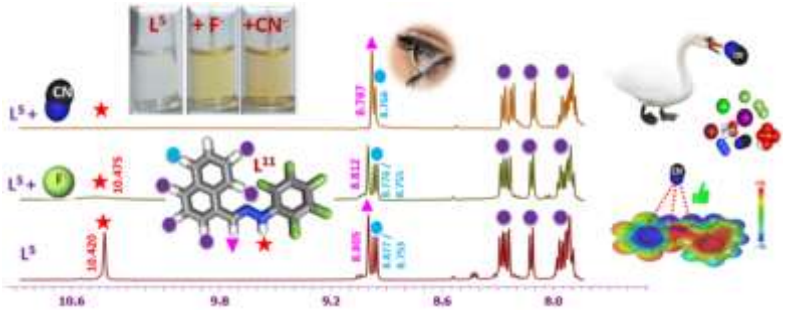

Figure 4: Graphical abstract of Molecular Swan

In our continuous effort given in the hunting of colorimetric cyanide selective anion receptor, herein we have successfully designed, synthesized, and characterized cyanide selective receptor**,** L^5. We have tested the colorimetric responses of sensor L^5 only the solution contains receptor L^5 with F^-, and CN^- ions show instant color change from colourless to faint brown and dark brown respectively. We have prepared a reference compound L^4. The only difference between the receptor L^5 and L^4 is presence of pentafluorophenyl moiety.

The binding efficiency of the sensor L^5 with cyanide and fluoride ion is calculated by UV-Vis spectrometric titration. The stoichiometric ratio is found to be 1:1 by job's plot. The association constants and LoDs are found to be 2.813 X 10^4 / 6 X 10^{-6} M and 2.284 X 10^4 / 3 X 10^{-6} M.

The observed selective sensing of receptor L^5 towards with cyanide and fluoride is further supported with MEP analysis. Unlike L^5, the reference receptor L^4 is intact with any other tested anions which strongly suggesting that the selectivity is mainly attributed due to the presence of electron deficient pentafluro phenyl moiety. The receptor L^5 is acts as "Molecular Swan". Swans are birds of the family Anatidae; the swan if offered a mixture of milk and water is said to be able to drink the milk alone. Similar way, if we offer mixture of various anions, the receptor L^5 is able to take only cyanide anion which is shown in Figure 4.

Chapter VII: Tuning the recognition properties of urea-based receptor towards cyanide in aqueous medium: Effect of fluorine substitution on strength and selectivity of the anion receptor

In this chapter, we have successfully tuned the selectivity and sensitivity of an anion receptor L^7 by substituting electron-withdrawing natured fluorine atoms directly onto the rim of the phenyl ring. Two fluorine substitutions made dramatic changes in the sensing ability as well as the selectivity of the receptor L^7 towards anions. The receptor L^7 senses fluoride, cyanide, acetate, and dihydrogen phosphate resulting in sudden color changes from yellow to brown; almost negligible spectral/color change for azide and bifluoride. We have also prepared a reference compound L^8 is substituted with only one fluoride atom and it colorimetrically senses fluoride, cyanide, acetate, and bifluoride.

Solution state binding studies of L^7 are carried out by UV–Vis spectrometry titration in 100% acetonitrile and it is found to be the receptor L^7 selectively binds cyanide, phosphate, and fluoride stronger than acetate. When we used an aqueous environment (10% of water in acetonitrile) as a testing solvent system, the receptor L^7 selectively sense cyanide ions are shown in figure 5. Overall, the strength of the receptor is increased towards anions with an increasing number of fluorine that of the receptor L^6 and L^7 has almost similar efficiency in binding towards acetate ion. Unlike receptor L^7, receptor L^8 does not

recognize $H_2PO_4^-$, but instead of $H_2PO_4^-$, it recognizes bifluoride as evidenced from UV–Vis spectroscopic and naked-eye colorimetric studies.

Change in the recognizing tendency of L^7 from L^8, towards F^-, CN^-, AcO^-, bifluoride, and dihydrogen phosphate might be due to the number of fluorine atoms present in the receptors (as well as nitro substitution on phenyl ring on L^7 and L^8). The inclusion of fluoro substitution on the phenyl rings of the receptor generates a positive electrostatic cloud and anion···π interaction, which might have played a crucial role in constructing a friendly atmosphere for the anion sensing.

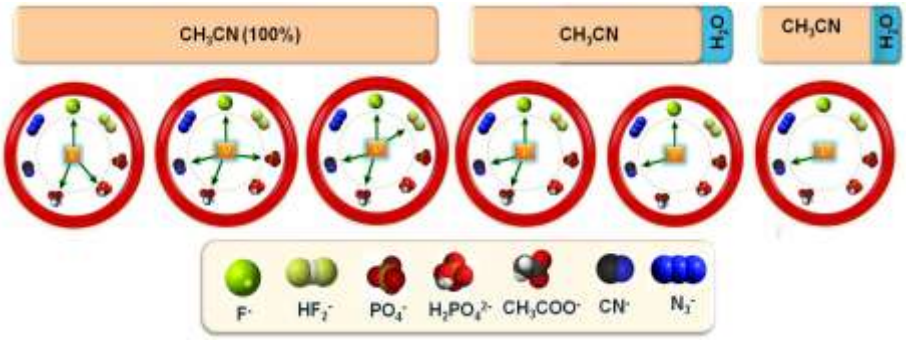

Figure 5: Graphical abstract of cyanide recognition in aqueous medium

Chapter VIII: Most Efficient Tris(3-Aminopropyl) Amine Based Electron Deficient Tripodal Receptor for Azide

In our continuing interest in the development of neutral receptors, we have decided to functionalize the more flexible tris (3-aminopropyl) amine with electron withdrawing natured fluoro phenyl moiety to get a suitable receptor. Since amide, sulfonamide, urea, and thiourea functionalities alter the selectivity and strength of the above-referred anion receptors, to find a better receptor for azide, herein, we have decided to incorporate the thiourea and amide functionality (in/as a single skeleton) extended hydrogen bond donor, tris (2-amino ethyl) amine and tris (3-amino propyl) amine as for C_3v cavity making the frame, and pentafluoro substituted benzene as an additional moiety for making anion-pi interaction. We have designed, synthesized an anion receptor L^{10} which shows the strongest binding towards azide anion. The sensing capabilities and selective affinities of receptors L^9 and L^{10} towards cyanide, acetate, and azide are supported and confirmed by colorimetric experiments.

The acetonitrile solution of L^9 and L^{10} with tetra butyl ammonium salts of cyanide, acetate, and azide yields immediate color change from faint-yellow to colorless. On under UV illumination, distinguishable blue emission was observed upon addition of cyanide, acetate, and azide with receptors L^9, and L^{10}.UV-Vis, ^{1}H- NMR, and IR spectroscopy studies indicate that both the receptors (L^9 & L^{10}) sensing azide anion colorimetrically bind azide anion stronger than any other anions such as acetate, and cyanide. In particular, the receptor L^{10} shows the highest binding strength towards azide anion. The MEP analyses to support our spectroscopic findings. The association constant and limits of detection for receptor L^{10} with azide are found to be $8.4X10^5$ M^{-1} and $3.16X10^{-6}$ M respectively. The observed highest binding strength of L^{10} with azide is could be due to the cooperative effect of extended traditional hydrogen bonding via thiourea amide functionality, anion-π interaction and C_3v suitable framework which is depicted in Figure 6. To the best of our knowledge, this is the first receptor showing the highest binding ability with azide anion.

Figure 6: Graphical representation of selectivity by a C_3v symmetric azide receptor and host: guest interaction

Chapter IX: Selective colorimetric sensing and perfect linear recognition of azide: Formation of Cu-azide-Cu cascade complex within the cavity of cryptand

Cryptand is one of the most promising candidates for the recognition of cations and anions since its cavity-forming ability. Among the cryptand family [15,21], aza-cryptand is initially known for cationic extraction, later extensively used to recognize the anionic species because of having hydrogen bond-making moieties and functionalizable secondary nitrogen atoms present in it. In 2006, Ghosh *et al.* has reported the first crystallographic evidence of a perfect linear recognition of azide inside the cavity of p-xylyl spaced bicyclic cryptand [30].

In continuation of searching the selective of receptors for a particular anion, herein, we are reporting a tris(3-amino propyl) amine TRPN based bicyclic aza-cryptand L^{11}, and copper complex of receptor L^{11} is turned into be a selective colorimetric chemosensor for a linear anion, azide. To the best of our knowledge, this is the first example of selective colorimetric sensing of azide by a trpn-capped cryptand-based bicyclic receptor.

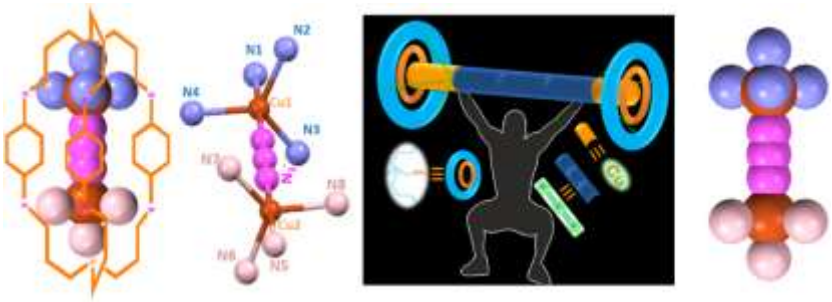

Figure 7: Schematic models for perfect linear recognition of azide inside the cavity through $N4^{-}\cdots N_3^{-}\cdots$Cu-N4 axle.

The colorimetric sensing capacity of complex 1 has been tested, 3:7 acetonitrile: water solution of complex 1 with TBA salt of azide results the immediate color change from faint blue to pale brown. The strength of the receptor towards azide anion is calculated by UV–Vis titration study. Solution state binding study of complex 1 results in the selective binding of azide anion with an association constant of $2.754\times10^{3}M^{-1}$ and to detect the azide ion as low as the concentration of 1.91×10^{-6} M, which is calculated from BH titrations and plot. Subsequently the stoichiometric ratio of cyanide: complex 1 is found to be 1:1 host: guest ratio.

In this work, we are illustrating the first example of selective colorimetric sensing of azide by a dicopper cryptate 1 via the ideal linear orientation of Cu-N_3^{-}-Cu axle inside the cylindrical shaped cavity. UV–Vis spectrometric studies reveal that complex 1 is binding azide anion more efficiently whereas there was no considerable binding observed with other tested anions which is shown in Figure 7. Incorporation of electron-deficient atoms on the aromatic moiety (for example fluoro substitution) of the chemosensor towards achieving exclusive selectivity of a particular anion in aqueous media is currently under investigation.

Chapter X: A molecular tuner: Substituent controlled π/π···hole induced selective colorimetric intramolecular push-pull fluoride sensor

Controlling the anion selectivity of synthetic anion receptors towards a particular anion is challenging task for researcher. In the case of bipodal receptors this become trickier since anion can approach the recognition elements of receptors from any direction. In order to overcome this problem, we adopted the new strategy in which the receptor molecules are functionalized with electron donating and/or withdrawing group. In the way of hunting such as receptors, L^{12} and L^{13} with electron withdrawing and donating groups have been synthesized for selective colorimetric anion sensing.

Figure 8: Graphical abstract of push-pull effect by withdrawing and donation substitution in L^{12} and L^{13}

Substituent effects on the strength of those receptors L^{12} and L^{13} have been studied by naked-eye colorimetric experiments, Ultraviolet-Visible spectrometric titration studies, FT-IR, ^{1}H NMR and MEP surface analysis. When we have nitro substitution on both end of the receptor L^{12}, there were no selectivity was found with anions and receptor L^{12} shows visible color change with the all the tested anions are shown in Figure 8. On the other hand, instead of nitro, when we have methyl substitution on one end and nitro substitution at an another end of the receptor L^{13}, it shows excellent selectivity towards fluoride ion with high association constant. Additionally, for azide considerable bathochromic shift of 70 nm was also observed with reference to absorption values of cyanide and fluoride anion which will clearly distinguish the presence of azide ion from cyanide and fluoride. The observed bathochromic shift is mainly attributed due to the intramolecular charge transfer (ICT).

In this work, we have successfully tuned the selectivity of synthesized receptors via generating a push-pull effect originated by electron withdrawing and donation substitutions on both end of the receptor L^{13}. The enhanced selectivity of L^{13} is achieved by altering the acidity of -NHs of L^{13} by substituting EW and ED groups.

Chapter XI: Summary and Conclusions

This chapter summarizes the results reported in chapter III - X and recommends the possible ways to improve the present studies for future research in this field.

Bryantsev and Hay *et al.* reported that, electron-withdrawing substituent on the aromatic systems appreciably increases the stability of anion-ligand complexes. Traditional hydrogen bond donors were assisted with π-hole moiety and obtained novel results in Fluoride, Cyanide, and Azide recognition. We have successfully prepared the first molecular phototropic system for cyanide L^1. This molecular phototropic system behaves like a molecular sunflower in which the conformation of this molecular sunflower is determined in response to the sunlight. This molecular sunflower can bind and sense the cyanide anion colorimetrically through its transition state, further upon exposure of this transition state cyanide complex under sunlight, this system is capable to release the bound cyanide to reach its lower energy stable state. In addition, the selectivity task was achieved by tuning the receptor parts. Dinitro part of L^1 was replaced with pentafluorophenyl unit.

The receptor L^2 shows a weak fluorescence emission spectrum which is mainly attributed due to the transfer of electron pair from the hydrazine(-NH) into highly conjugated pyrene fluorophoric unit. In this report the receptor L^2 sense exclusively cyanide anion via Photo Electron Transfer (PET) mechanism.

We have designed, synthesized and studied the anion binding properties of di-nitro substituted electron deficient imine based receptor L^3 and it colorimetrically senses cyanide ion. A detailed molecular electrostatic potential map analysis supports our spectroscopy findings. The aryl group having nitro functionalities that contributes to anion binding in cyanide complex of L^3 through CH•••cyanide ion interactions. The

preferential cyanide binding by receptor L^3 predominantly attributed due to enriched aromatic C–H•••anion and imine-CH•••anion interactions. To the best of our knowledge this is a first report of colorimetric sensing of cyanide majorly inclined by non-traditional aromatic -C–H•••cyanide interaction.

We have successfully designed, synthesized and characterized cyanide selective receptor L^5, by incorporating electron deficient functional group as a part of receptor became most proficient strategy in the sensor design. Unlike L^5**,** the reference receptor L^4 is intact with any other tested anions which strongly suggesting that the selectivity of L^5 towards cyanide ion is mainly attributed due to the presence of electron deficient pentafluoro phenyl moiety in the receptor.

In designing the receptors, it would be desirable to enhance the positive charge in the benzene ring of L^6 for their involvement in anionic guest interactions and other nonbonding interactions that ultimately might produce a more efficient receptor towards a particular anion. In this connection, to see the effect of the electron-withdrawing substitution, at the one end of L^7, we have decided to substitute electron-withdrawing natured fluorine atoms on the phenyl ring. It is expected the receptor L^7 to be more efficient in terms of binding and/or selectivity towards anions than L^6. One/two fluorine(s) substitutions made a dramatic change in the sensing ability, as well as the selectivity of the receptor. The inclusion of fluoro substitution on the phenyl rings of the receptor L^7 generates a positive electrostatic cloud and anion$\cdots\pi$ interaction, which might have played a crucial role in constructing a friendly atmosphere for selective cyanide ion sensing in semi-aqueous media.

We have designed, synthesized an anion receptor L^9 & L^{10} by incorporate the thiourea and amide functionality (in/as single skeleton) extended hydrogen bond donor, tris(2-amino ethyl) amine and tris (3-amino propyl) amine as for C_3v cavity making frame, and pentafluoro substituted benzene as an additional moieties for making anion-pi interaction. From this results, L^{10} which shows the strongest binding towards azide anion. To the best of our knowledge this is the first receptor showing the highest binding ability with azide anion. The observed highest binding strength of L^{10} with azide is could be due to the cooperative effect of extended traditional hydrogen bonding via thiourea-amide functionality, anion-π

interaction, and C_{3v} suitable framework.

In continuation of searching the selective of receptors for a particular anion, herein, we are reporting a tris (3-amino propyl) amine TRPN based bicyclic aza-cryptand L^{11}, and copper complex of receptor L is turned into be a selective colorimetric chemosensor for a linear anion, azide. To the best of our knowledge, this is the first example of selective colorimetric sensing of azide by a trpn-capped cryptand-based bicyclic receptor. This is the first example of selective colorimetric sensing of azide by a dicopper cryptate 1 via the ideal linear orientation of Cu-N_3^--Cu axle inside the cylindrical shaped cavity.

In the X chapter, we have tuned the selectivity of receptor via intramolecular push-pull effect by electron withdrawing and donating substituent.

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7. LIST OF PUBLICATIONS

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